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**THE KINETICS OF THE SINTERING OF HOT PRESSED  
MOLYBDENUM DISULFIDE AND MOLYBDENUM DISULFIDE-  
SILVER COMPOSITIONS AND THE EFFECT ON THE  
ELECTRICAL CONDUCTION PROCESSES**

by DONALD R. ULRICH AND HARRY M. KING  
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In cooperation with the Technology Utilization Office

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Space Flight Center,  
Huntsville, Alabama*

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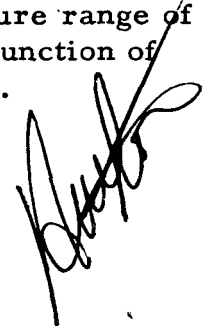
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ABSTRACT

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The hot pressing kinetics of molybdenum disulfide and molybdenum disulfide-silver compositions, which are of interest as electrical conductors in a vacuum, have been studied. The rate of sintering is described by the first-order rate equation of Murray et al. as being a molybdenum disulfide controlled plastic flow mechanism. The diffusion of silver is a second process occurring over the temperature range of hot pressing. The electrical conduction mechanism as a function of both composition and fabrication temperature is discussed.



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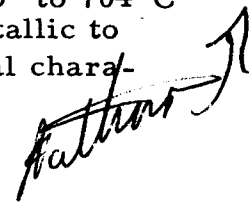
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## TECHNICAL MEMORANDUM X-53111

# THE KINETICS OF THE SINTERING OF HOT PRESSED MOLYBDENUM DISULFIDE AND MOLYBDENUM DISULFIDE- SILVER COMPOSITIONS AND THE EFFECT ON THE ELECTRICAL CONDUCTION PROCESSES

### SUMMARY

The hot pressing kinetics of molybdenum disulfide and molybdenum disulfide-silver compositions, which are of interest as electrical brush materials in a vacuum, have been studied. The rate of sintering is described by the first-order rate equation of Murray et al. as being a molybdenum disulfide controlled plastic flow mechanism. The diffusion of silver is a second process occurring over the temperature range of hot pressing. The electrical conduction mechanism is a function of both composition and fabrication temperature. The transition from the non-metallic conduction process, characteristic of molybdenum disulfide, to that of metallic silver occurs within the range of 13.8% to 26% of silver. The non-metallic conduction occurs through positive hole conduction. A 55.9% MoS<sub>2</sub>-44.1% Ag composition, hot pressed at temperatures of 593° to 927° C (1100° - 1700° F) and at 3500 psi, had non-metallic conduction up to 680° C (1256° F). In the vicinity of 680° to 704° C (1256° - 1300° F), the conduction process changed from non-metallic to metallic. At 927° C (1700° F), the composition had the electrical characteristics of a degenerate semiconductor.



### INTRODUCTION

Graphite electrical contact brushes containing metallic halide additives utilized in high altitude aircraft do not perform satisfactorily in a space environment. They were designed to operate with reasonable overhaul life in atmospheres of low oxygen and low water vapor content and will not function properly in vacuum. This has led to a program at Marshall Space Flight Center to develop and evaluate other materials. These materials included molybdenum disulfide compositions containing metallic additives. The molybdenum disulfide has the hexagonal platelet structure of graphite, but the bonding of the layers is dependent upon forces other than those of the absorbed gases and water as in graphite. Consequently, molybdenum disulfide maintains its structure in a vacuum and provides the requisite lubricity for electrical contact brushes operating in a space environment. The metallic additives provide the required electrical conductivity.



The evaluation of hot pressed molybdenum disulfide and metallic powder compositions for use as electrical contact brushes in vacuum has been reported by Horton (Ref. 1 and 2). The materials development program and hot pressing procedures used for fabricating these materials have been described by King (Ref. 3). Compositions of hot pressed molybdenum disulfide containing metallic silver have shown promise. Long periods of wear life have been obtained with a particular composition, but the results have not been reproducible since the periods of wear life vary from specimen to specimen.

An analysis of the variation in wear life of the hot pressed molybdenum disulfide-silver compositions has been reported by Ulrich (Ref. 4). The variation in wear life of a 55.9% MoS<sub>2</sub> - 44.1% Ag (wt) composition was analyzed to determine the contribution of brush composition (and processing to failure and the mechanisms of failure). The wear life of the brushes was determined to vary inversely with the volume of free silver at the wear surfaces. The variable silver concentration in the brush specimens was due to an irregular silver distribution in the hot pressed slugs from which the brushes were cut. It was determined that this occurred predominantly from migration of the silver during hot pressing.

The findings of the analysis indicated that further study of the ceramic properties of molybdenum disulfide and molybdenum disulfide containing silver additions was necessary. In this investigation, a study of the hot pressing kinetics of molybdenum disulfide and molybdenum disulfide containing silver additions was undertaken. The adaptability of a plastic flow model for explaining the sintering process has been tested. The nature of the silver migration process over the temperature range of hot pressing was determined. The electrical conduction properties as a function of fabrication temperature and of compositions and temperature are described herein. For a better understanding of the recently acquired data presented in this report, a few of the results of the analysis (Ref. 4) and the hot pressing procedure (Ref. 3) have been restated.

#### ACKNOWLEDGMENT

Appreciation is expressed to Messrs. W. L. Prince and H. W. Smith for their help with the X-ray and microscopic work, respectively.

## EXPERIMENTAL PROCEDURE

Commercial grade molybdenum disulfide supplied by the McGee Chemical Company and silver from the Martin-Marietta Corporation were used in pressure sintering. Compositions containing up to and including 57.4% (wt) silver were hot pressed at 3500 psi and 927° C (1700° F). A composition of 55.9% molybdenum disulfide and 44.1% silver was hot pressed at 3500 psi and temperatures of 593° C (1100° F), 680° C (1256° F), 704° C (1300° F), 732° C (1350° F), 760° C (1400° F), 815° C (1500° F), 871° C (1600° F) and 927° C (1700° F). The powdered sample and graphite mold were placed in a cold furnace, and pressure was applied before heating. The time interval during isothermal pressing was measured from the time of attainment of the desired temperature until the release of pressure.

For electrical conductivity measurements, rectangular specimens were cut and machined from the hot pressed specimens in the dimensional ratio of thickness: width: length of 1:3:9. The specimens were cut so that l and w were in the plane normal to the direction of applied pressure. The specimens were electroded with a fired-on silver preparation so that the potential probe or "four point" method for measuring electrical resistivity could be utilized. This method eliminates the errors that could be introduced by stray electromotive forces at the electrode interfaces. The surface conductivity of fired-on silver is much higher than that of air-dried silver. The resistance was measured on a Keithley Model 503 Milliohmmeter. The resistivity and conductivity were calculated as functions of temperature.

The crystalline phases present and the silver distribution over both the temperature and compositional range of hot pressing were examined by X-ray techniques and reflected light microscopy.

## RESULTS AND DISCUSSION

The relative density of specimens hot pressed at 927° C (1700° F) is plotted against silver content in FIG 1, which shows that the relative density increases with increased silver. The increase in relative density with rising temperature for the 100%, 74%, and 55.9% molybdenum disulfide compositions while under pressure is shown in FIG 2. The electrical conductivity of the specimens hot pressed at 927° C (1700° F) as a function of silver content is shown in FIG 3. Hexagonal molybdenum disulfide coexists with metallic silver in these bodies. No minor

crystalline phases such as silver sulfide were detected when the specimens were exposed for 15 hours, using the Debye Scherrer technique.

The electrical conductivities as a function of temperature are plotted in FIG 4. The conductivities of the 100% and 86.2% MoS<sub>2</sub> bodies lie within the same order of magnitude. Both follow an Arrhenius plot, having the negative coefficients of resistivity or positive coefficients of conductivity which are characteristic of non-metallic conduction. The activation energies of the 100% and 86.2% MoS<sub>2</sub> compositions are 0.27 and 0.20 eV, respectively. Hall effect measurements show that these compositions are p type semiconductors, the dominant conduction process being through hole conduction.

The non-metallic to metallic conduction transition occurs within the volume range of 13.8% to 26% of silver. A composition of 74% MoS<sub>2</sub> had a negative coefficient of conductivity, the slope of the plot being the same as that of metallic silver.

Several test specimens were cut from hot pressed slugs of the 55.9% MoS<sub>2</sub> composition. The room temperature resistivities varied from 10<sup>-5</sup> to 10<sup>-3</sup> ohm-cm, which are in between those of good semiconductors and conductors (FIG 4). They have positive temperature coefficients of resistivity and can be classified as degenerate semiconductors. The specimens of high conductivity have been found to have a higher silver content than those of lower conductivity. This indicates an irregular silver distribution in the hot pressed 55.9% MoS<sub>2</sub> samples. The silver was well distributed throughout unfired dry pressed samples. When dry pressed samples were sintered in an electric kiln at 927° C (1700° F), it was determined that the silver migrated to the lower surface of the specimens (relative to their position in the kiln); the upper surface was rich in MoS<sub>2</sub>. Thus, excessive silver migration occurs when the 55.9% MoS<sub>2</sub> composition is fired in the absence of increased pressure.

This excessive silver migration did not occur when the compositions were hot pressed, but there was some redistribution. In the specimens that were hot pressed at 3500 psi at lower temperatures, the redistribution increased with increasing processing temperature so that by 927° C (1700° F) the irregularity was sufficient to produce variations in electrical conductivity. Light microscopy shows that the silver is distributed in localized concentrations throughout a molybdenum disulfide matrix. This suggests that during hot pressing there is a migration of silver to the locations of lowest free energy. Diffusion flow is responsible for the sintering of metallic silver (Ref. 5).

The rate equation of Murray, Livey, and Williams (Ref. 6) for describing the pressure sintering of ceramics was tested to determine if it would describe the hot pressing of the molybdenum disulfide-silver compositions using the experimental results of the 55.9% MoS<sub>2</sub> -44.1% Ag compositions. This equation is representative of the hot pressing of aluminum oxide (Ref. 7) and fused silica (Ref. 8). The rate equation has the form of a first-order kinetic curve

$$\frac{dD}{dt} = \frac{3P}{4\eta} (1-D)$$

where D is the relative density, P is the applied pressure, and  $\eta$  is the viscosity. Integration gives

$$\ln (1-D) = \frac{3}{4} \frac{P}{\eta} t + C.$$

A plot of  $\ln (1-D)$  versus time t should give a straight line from which the viscosity can be calculated for isothermal pressing. This relation was substantiated in the present study. The isothermal plots of  $\ln (1-D)$  versus time are given in FIG 5. Since the rate equation is based on the flow characteristics of a Bingham body, the pressure effect on the rate of sintering is controlled by a plastic flow mechanism. The viscosity of the 55.9% MoS<sub>2</sub> composition at 927° C (1700° F) is the same as that of 100% MoS<sub>2</sub> (FIG 5), which indicates that the density is controlled by the molybdenum disulfide. A plot of the log of the viscosity versus the reciprocal of absolute temperature is shown in FIG 6. This suggests that the sintering mechanism is a thermally activated process, the activation energy being 18.7 kcal per mole. Since X-ray and microscopy have shown a silver migration, a silver diffusion mechanism is accompanying the plastic flow mechanism of the molybdenum disulfide.

The conductivity-temperature measurements of the 55.9% MoS<sub>2</sub> bodies with hot pressing temperatures over the range of 593° to 877° C (1100° - 1612° F) are shown in FIG 7. The room temperature conductivity increases with increased fabricating temperature. With fabricating temperatures in the vicinity of 680° to 704° C (1256° - 1300° F), the conduction process changes from non-metallic to metallic; i. e., the conduction process is characteristic of metallic silver. The slope  $\left( \frac{\ln \sigma}{1/T} \right)$  of the 593° C (1100° F) body is nearly the same as that of 100% MoS<sub>2</sub>.

The change to non-metallic conduction is abrupt; the transition temperature has varied between  $680^{\circ}$  to  $704^{\circ}\text{C}$  ( $1256^{\circ}$  -  $1300^{\circ}\text{F}$ ) in different trials.

## CONCLUSIONS

The first-order rate equation of Murray et al. has been experimentally verified, indicating that the rate of sintering is described by a molybdenum disulfide controlled plastic flow mechanism. A second mechanism occurring over the temperature range of hot pressing is the diffusion flow of silver. The transition from the non-metallic conduction process, characteristic of molybdenum disulfide, to that of metallic silver occurs within the range of 13.8% to 26% of silver. The non-metallic conduction occurs through positive hole conduction. A 55.9%  $\text{MoS}_2$  - 44.1% Ag composition, hot pressed at temperatures of  $593^{\circ}$  to  $927^{\circ}\text{C}$  ( $1100^{\circ}$  -  $1700^{\circ}\text{F}$ ) and at 3500 psi, had non-metallic conduction up to  $680^{\circ}\text{C}$  ( $1256^{\circ}\text{F}$ ). In the vicinity of  $680^{\circ}$  to  $704^{\circ}\text{C}$  ( $1256^{\circ}$  -  $1300^{\circ}\text{F}$ ), the conduction process changed from non-metallic to metallic. At  $927^{\circ}\text{C}$  ( $1700^{\circ}\text{F}$ ), the composition had the electrical characteristics of a degenerate semiconductor.

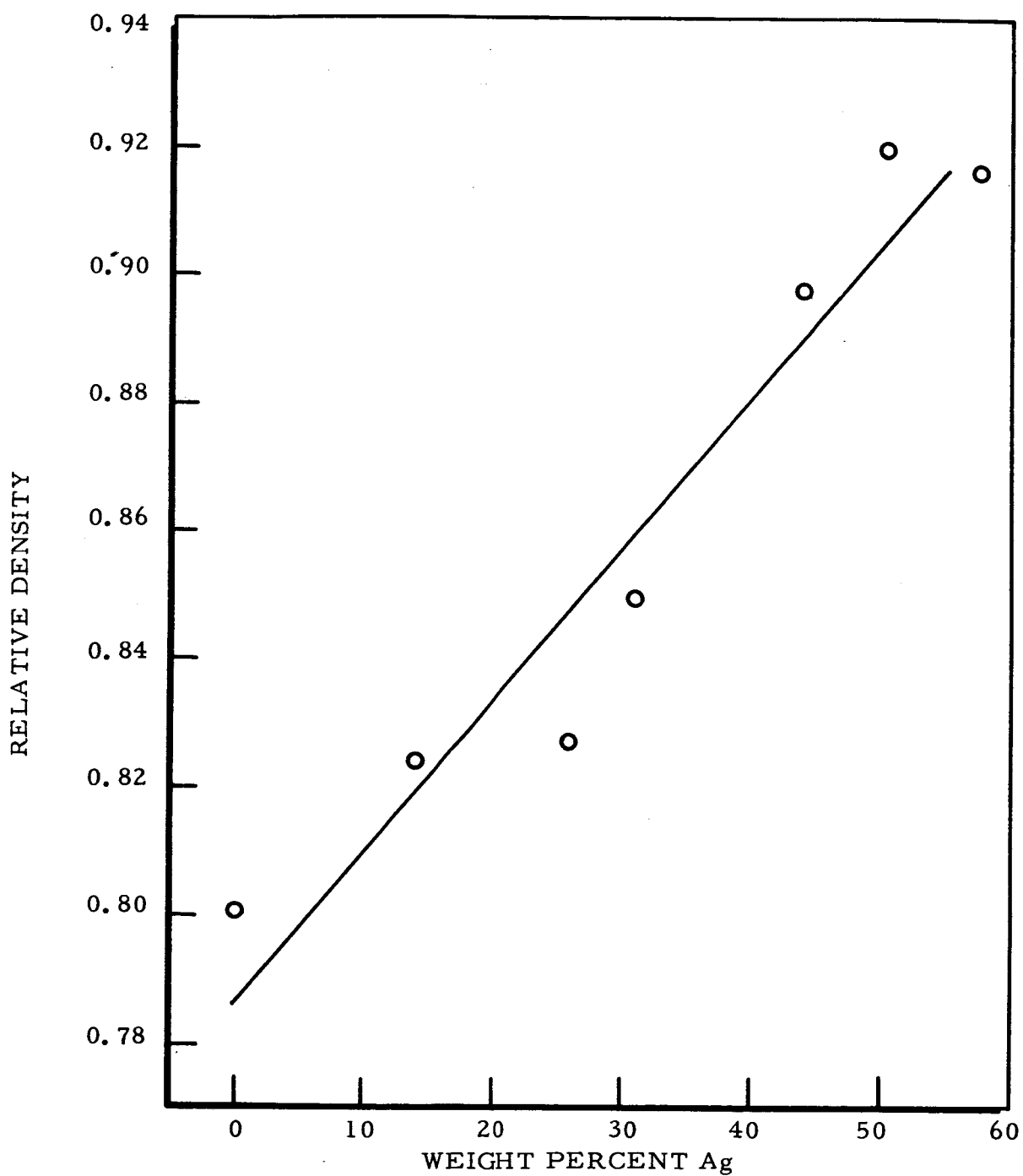


FIGURE 1. Relative End-Point Density as a Function of MoS<sub>2</sub>-Ag Hot Pressed at 927°C and 3500 PSI

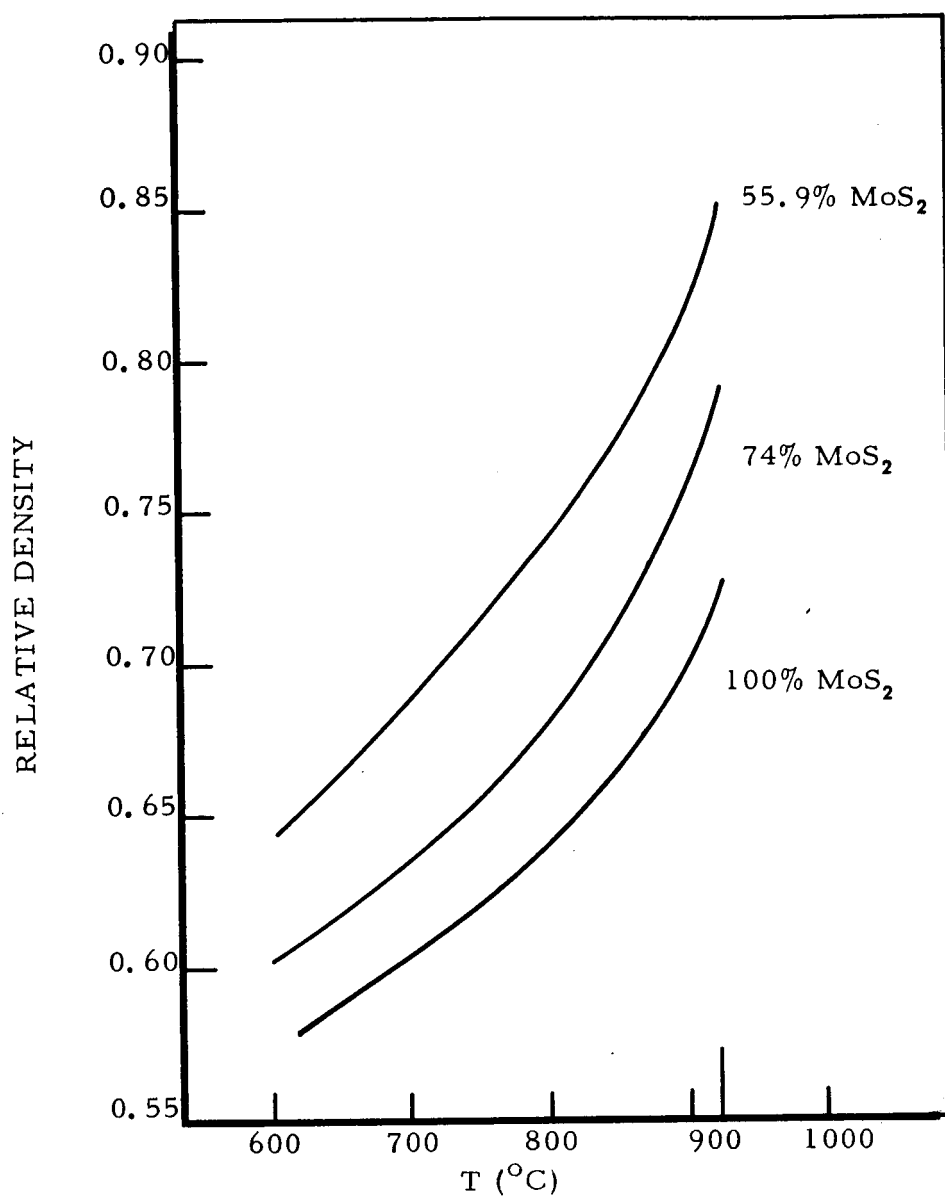


FIGURE 2. Relative Density of the 100%, 74%, and 55.9% MoS<sub>2</sub> Compositions Versus Temperature During Hot Pressing

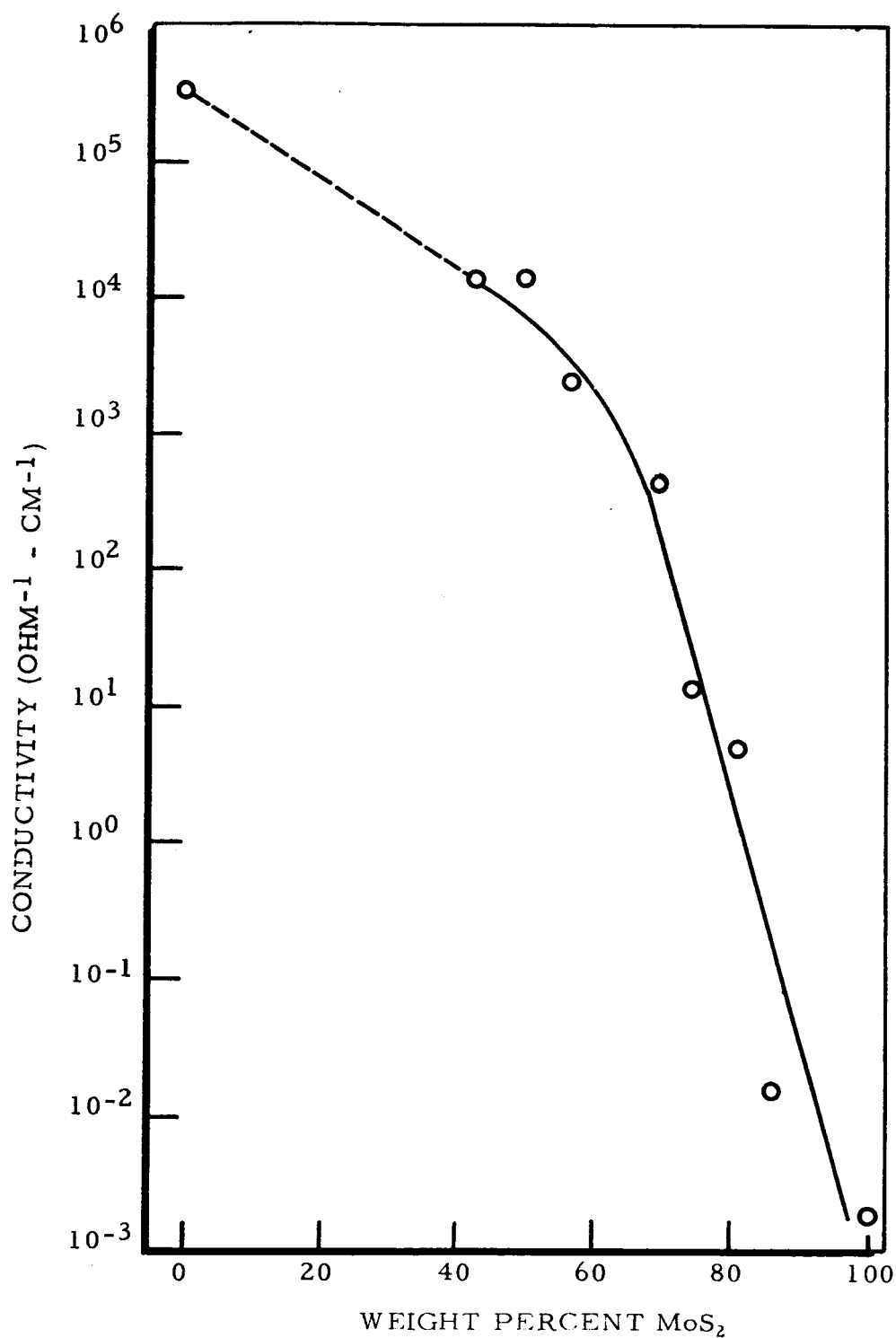


FIGURE 3. Conductivity as a Function of Composition of  $\text{MoS}_2$  - Ag Hot Pressed at  $927^\circ\text{C}$  and 3500 psi



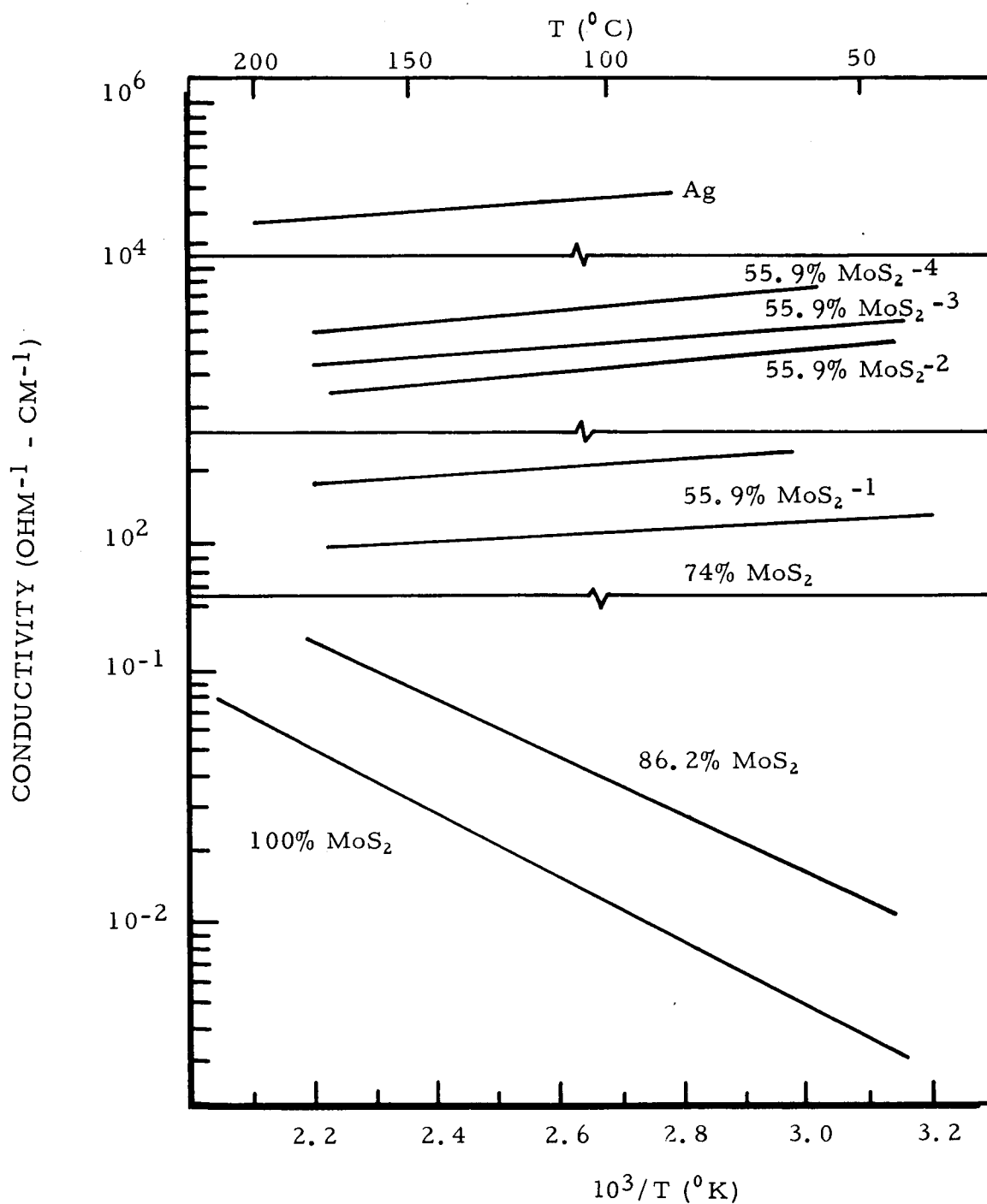


FIGURE 4. Conductivity as a Function of  $1/T$  for  $\text{MoS}_2$ -Ag Compositions Hot Pressed at  $927^{\circ}\text{C}$  and 3500 psi.

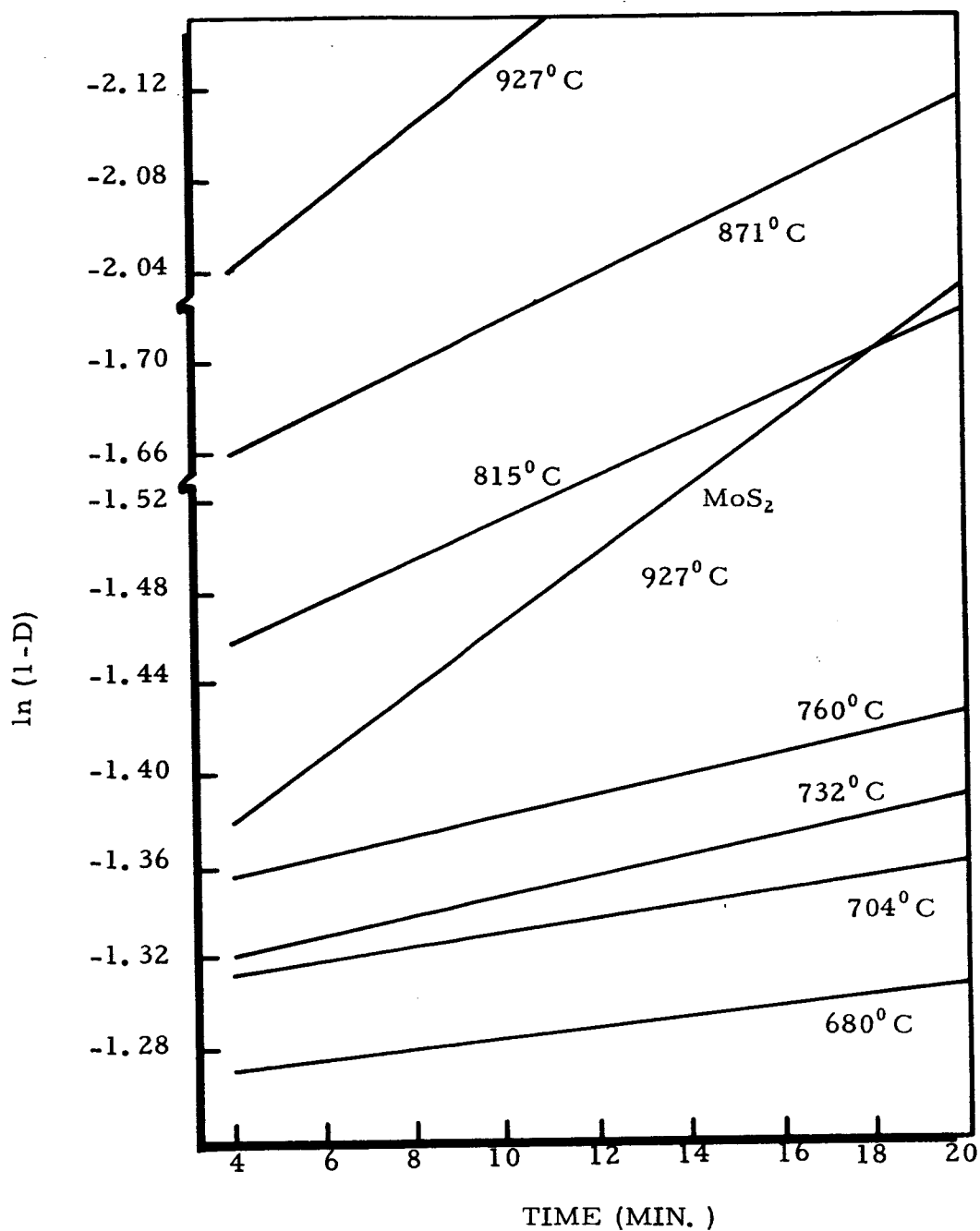


FIGURE 5. Plot of  $\ln(1-D)$  as a Function of Time and Fabricating Temperature for Hot Pressed MoS<sub>2</sub> and 55.9% MoS<sub>2</sub> - 44.1% Ag Compositions

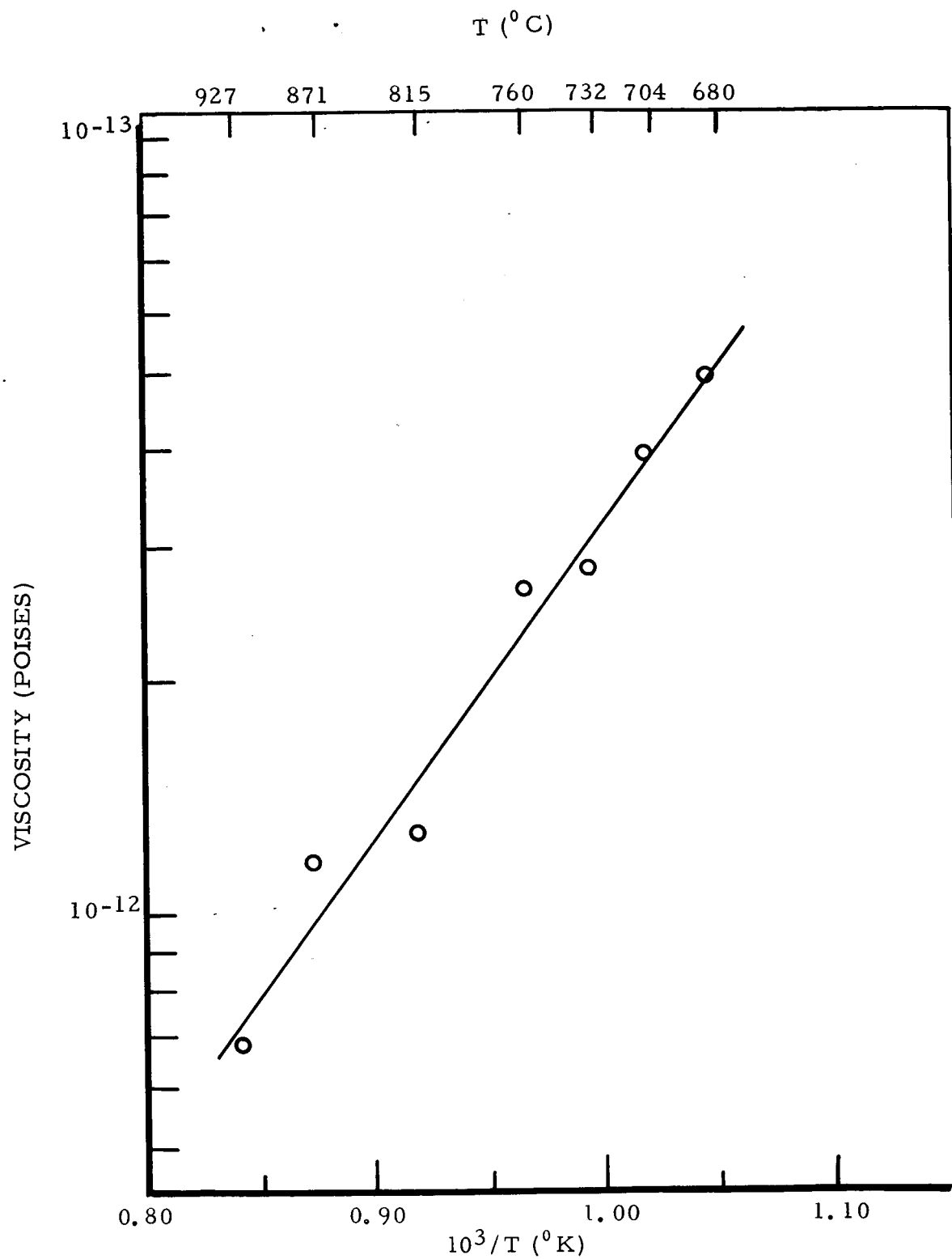


FIGURE 6. Viscosity as a Function of  $1/T$  and Fabricating Temperature for Hot Pressed  $\text{MoS}_2$  and 55.9%  $\text{MoS}_2$  - 44.1% Ag Compositions

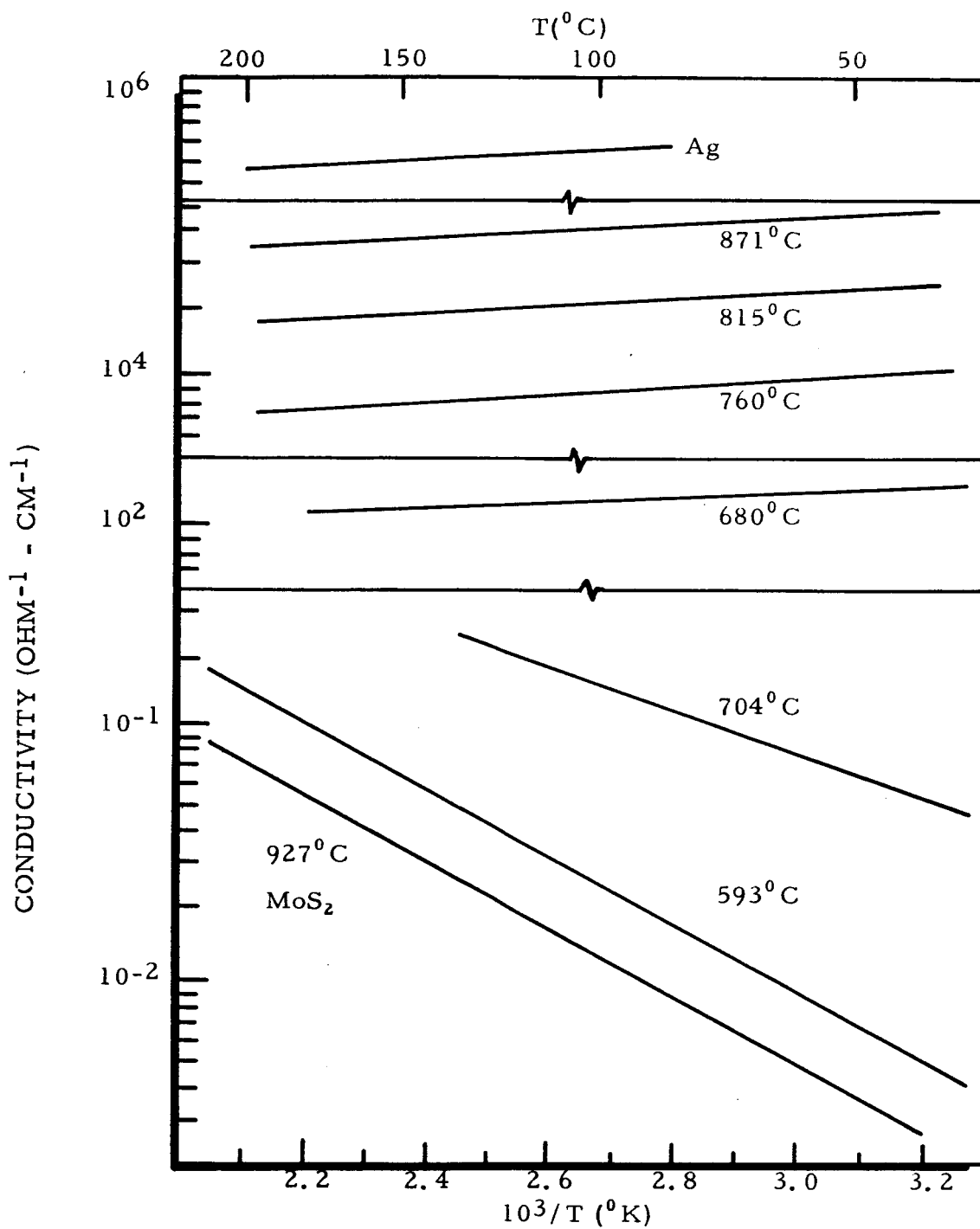


FIGURE 7. Conductivity as a Function of  $1/T$  for MoS<sub>2</sub> and 55.9% MoS<sub>2</sub> - 44.1% Ag Composition Hot Pressed at Temperatures from 593°C to 871°C

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This document has also been reviewed and approved for technical accuracy.

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